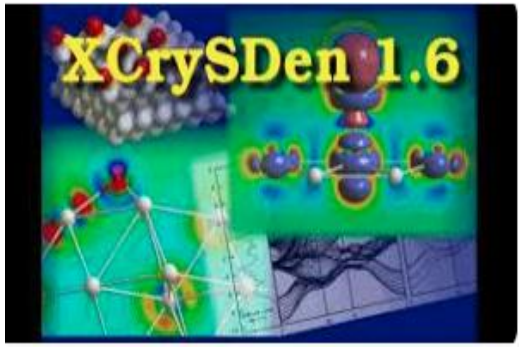


DOCTORAL SEMINAR

Presentation on:

MATERIALS MODELLING USING DENSITY FUNCTIONAL THEORY (DFT)

QUANTUMESPRESSO

EPW®

By WAH KENOUNOUH Lavoisier Junior

REPUBLIQUE DU CAMEROUN

Paix-Travail-Patrie
****
UNIVERSITE DE DSCHANG
****
FACULTE DE SCIENCE
****
ECOLE DOCTORALE

REPUBLIC OF CAMEROON

Peace-Work-Fatherland
****
UNIVERSITY OF DSCHANG
****
FACULTY OF SCIENCE
****
POST GRADUATE SCHOOL

DSCHANG SCHOOL OF SCIENCE AND TECHNOLOGY

UNITE DE RECHERCHE DE MATIERE CONDENSEE D'ELECTRONIQUE ET DE TRAITEMENT DE SIGNAL (UR-MACETS)

Topic:

DENSITY FUNCTIONAL THEORY: INTRODUCTION TO QUANTUM ESPRESSO AND ELECTRON PHONON WANIER CODE

By WAH KENOUNOUH Lavoisier Junior

Under the supervision of :

LUKONG FAI Cornelius **&** ***DIFFO TCHINDA Jaures***

Full Professor *Associate Professor*

CONTENTS

- Introduction
- Theoretical DFT
- Derivation of the Kohn-Sham equation
- Computational DFT: Si atom
- Case of Ni, Cu, FeO, and GaAs
- Software packages
- Feynman density matrix approaches
- Conclusion

INTRODUCTION

One of the basic problems in theoretical physics and chemistry is the description of the structure and dynamics of many-electron systems. DFT is a method of quantum calculation that enable the study of the electronic structure in a more exact way. At the beginning of the XXI century DFT is one of the must used method in the condensed matter Physics as well as in Chemistry because of it wide applications.

INTRODUCTION

As the road is paved towards more performing algorithms and quantum information processing, the technics of modelling in a more exact manner materials at an atomic scale have becomes more accurate. It is nowadays possible to characterize faithfully a lot of materials using methods base on the fundamental laws of quantum mechanics and electromagnetism. Although the practical study of those complex system requires some approximations, the results doesn’t depends on any adjustable parameter: this is why these technics are called *ab initio* calculus or first principle calculations.

THEORETICAL DFT:

HOHENBERG AND KOHN THEOREM
AND
KOHN-SHAM EQUATION

Generalities on DFT

Historically the birth date of DFT coincides with a manuscript published by Hohenberg and Kohn in 1964 in the journal Physical Review, entitled ‘Inhomogeneous electron gas’. The traditional methods in the electronic structure theory, particularly the Hartree-Fock theory and the derived methods are base on the multielectronic wavefunction. The main idea of DFT is to replace the multielectronic wavefunction by the electronic density as base quantity for all the calculations. Since the multielectronic wavefunction depends on 3N varaibles the density only depends on three variables so , with the help of DFT we move from a 3N dimensional equation to N equations of Three dimension.

The principle of DFT consist of a reformulation of a quantum problem of N-bodies at a one-body or two body problem with the electronic density of the ground state being the only parameter that determines all the observable of the system.

Hohenberg and Kohn theorem

The starting point of any discussion of DFT is the Hohenberg-Kohn (HK) theorem. It represents the most basic of a number of existence theorems which ensure that stationary many-particle systems can be characterized (fully) by the ground state density and closely related quantities.

First: The ground state of any interacting many particle system with a given fixed inter-particle interaction is a unique functional of the electronic density.

$$E = F[\mathrm{n}] \qquad (1)$$

Second: The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solutions of the Schrodinger equation

$$\left.\frac{\delta F[\mathrm{n}]}{\delta n}\right|_{n_0} = 0 \qquad (2)$$

KOHN-SHAM EQUATION

1- The many-electron Schrodinger equation:

$$\left(KE + PE\right)\Psi = E_{tot}\Psi \qquad (1)$$

2- Clamped nuclei approximation (Born-Oppenheimer):

$$-\sum_{I=1}^{M}\frac{\nabla_I^2}{2M_I} \to 0 \qquad \frac{1}{2}\sum_{I\neq J}^{M}\frac{Z_I Z_J}{\left|\vec{R}_I - \vec{R}_J\right|} = cte \qquad \Psi = \Psi\left(\vec{r}_1,...,\vec{r}_N\right) \qquad (2)$$

3- Independent electrons approximation:

$$\frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{\left|\vec{r}_i - \vec{r}_j\right|} = 0 \quad and \quad \Psi = \Psi\left(\vec{r}_1,...,\vec{r}_N\right) = \phi_1\left(\vec{r}_1\right)\times\cdots\times\phi_N\left(\vec{r}_N\right) \qquad (3)$$

4- Hartree-Fock or self-consistent field approximation

$$\Psi(\text{ground state}) \equiv \textit{Slater}\ \text{determinant} \qquad (4)$$

5- Mean-field approximation:

$$PE = V_n(\vec{r}) \rightarrow PE = V_n(\vec{r}) + V_H(\vec{r}) \tag{5}$$

6- Hartree-Fock equations:

❖First, we suppose that electrons do interact indeed, but perhaps this interaction is not too strong. This introduces a local exchange potential $V_X(\vec{r},\vec{r}')$.

❖Second, owing the Coulomb repulsion one has:

$$\left|\Psi(\vec{r}_1,\vec{r}_2)\right|^2 \prec \left|\phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\right|^2$$
$$\Downarrow \tag{6}$$
$$V_c(\vec{r})$$

Which yields the Kohn-Sham equation:

$$\left[-\frac{\nabla^2}{2} + V_n(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r})\right]\phi_i(\vec{r}) = \varepsilon_i\phi_i(\vec{r}) \tag{7}$$

Where the last potential is determine within the LDA or LSDA and the GGA.

COMPUTATIONAL DFT:

QUANTUM ESPRESSO (QE)
AND
ELECTRON PHONON WANIER CODE (EPW)

Case of Silicon atom

GNU nano 4.8 Si.pwscf.in Modified

```
&CONTROL
  calculation = 'scf',
  prefix = 'silicon',
  outdir = './',
  pseudo_dir = './',
  verbosity = 'high'
/

&SYSTEM
  ibrav =  2,
  celldm(1) = 10.26,
  nat =  2,
  ntyp = 1,
  ecutwfc = 30
  nbnd = 8
/

&ELECTRONS
  mixing_beta = 0.6
/

ATOMIC_SPECIES
  Si 28.086 Si.pz-vbc.UPF

ATOMIC_POSITIONS (alat)
   Si       0.000000000  -0.000000000  -0.000000000
   Si       0.248675487   0.248675487   0.248675487

K_POINTS (automatic)
  6 6 6 0 0
```

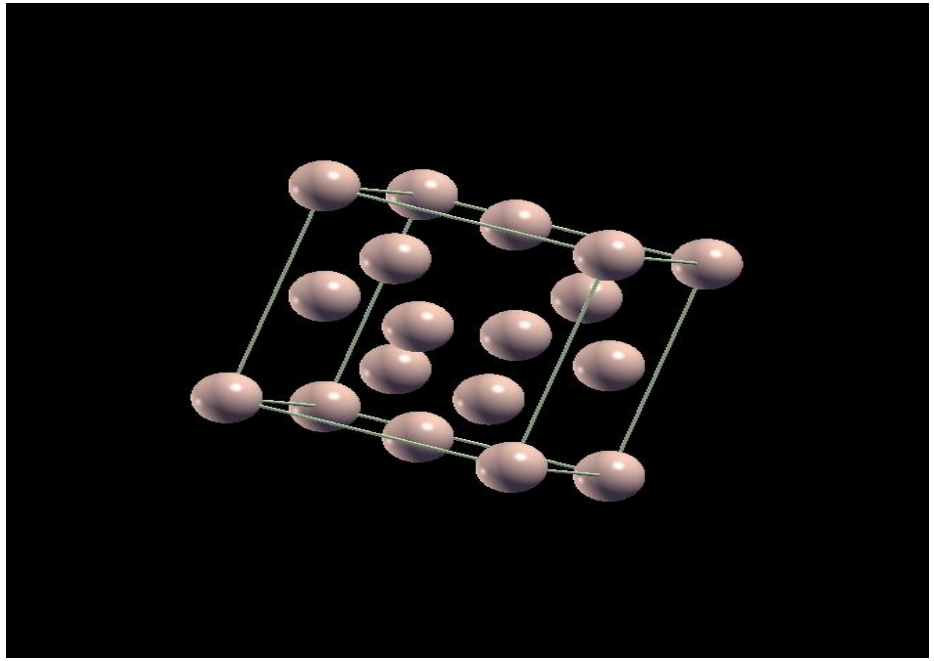
^G Get Help ^O Write Out ^W Where Is ^K Cut Text ^J Justify
^X Exit ^R Read File ^\ Replace ^U Paste Text ^T To Spell

GNU nano 4.8 Si.bands.in Modified

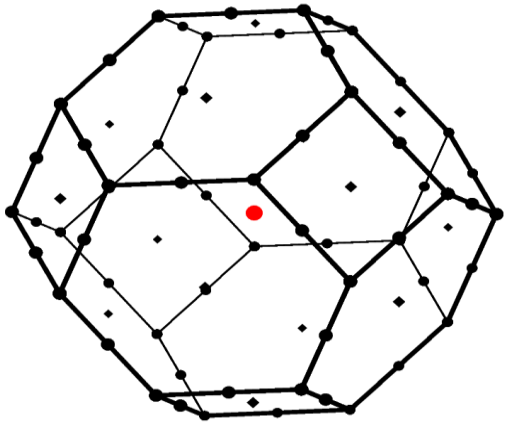
```
#Description of the input file
   #we want to perform self consistent field calculation (scf)
   #prefix is reference to the output files
   #output directory where all the calculations output will be stored (outdir)
   #directory where the PP is located, by puting './' we maen the PP is located in the current directory (pseudo_dir)
   #high verbosity means more details in the output file
   #Bravais lattice index, to precise if sure at 100% of the structure of the material, if not take ibrav=0 and precise the cel>
   #lattice constant in Bhor (celldm(i)) or in Agnstrom (A, B...): 1 Bohr = 0.529177249 Å and 1 Rydberg (Ry) = 13.6056981 eV.
   #Mixing factor used in the self-consistent method (mixing_beta)
&CONTROL
  calculation = 'bands',
  prefix = 'silicon',
  outdir = './',
  pseudo_dir = './',
  verbosity = 'high'
/

&SYSTEM
  ibrav =  2,
  celldm(1) = 10.26,
  nat =  2,
  ntyp = 1,
  ecutwfc = 50
  ecutrho = 400
  nbnd = 8
/

&ELECTRONS
  conv_thr = 1e-8
  mixing_beta = 0.6
/

ATOMIC_SPECIES
  Si 28.086 Si.pz-vbc.UPF

ATOMIC_POSITIONS (alat)
   Si       0.000000000  -0.000000000  -0.000000000
   Si       0.248675487   0.248675487   0.248675487

K_POINTS {crystal_b}
  5
    0.0000 0.5000 0.0000 20  !L
    0.0000 0.0000 0.0000 30  !G
    -0.500 0.0000 -0.500 10  !X
    -0.375 0.2500 -0.375 30  !U
    0.0000 0.0000 0.0000 20  !G
```

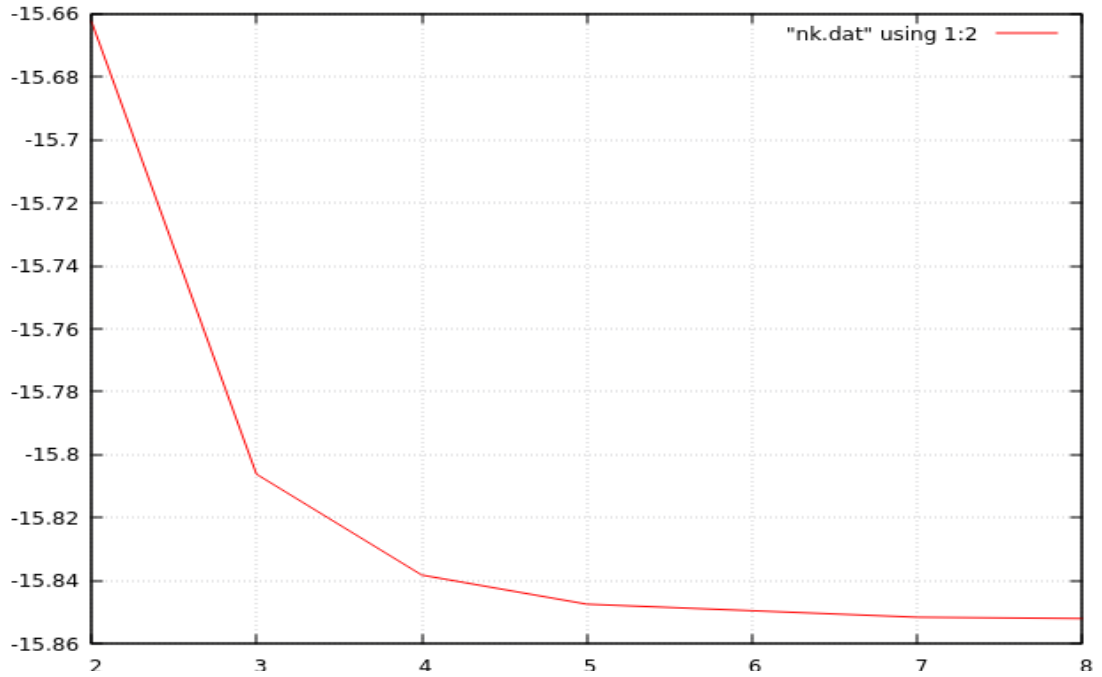
^G Get Help ^O Write Out ^W Where Is ^K Cut Text ^J Justify ^C Cur Pos M-U Undo M-A Mark Text
^X Exit ^R Read File ^\ Replace ^U Paste Text ^T To Spell ^ Go To Line M-E Redo M-6 Copy Text

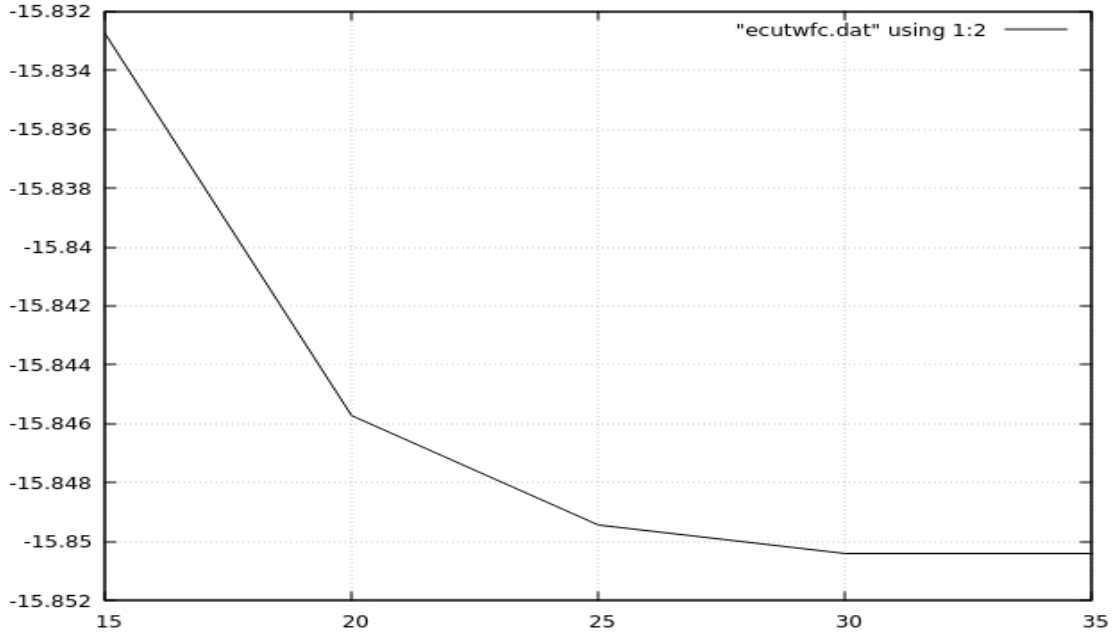
QE input files for scf and band calculation



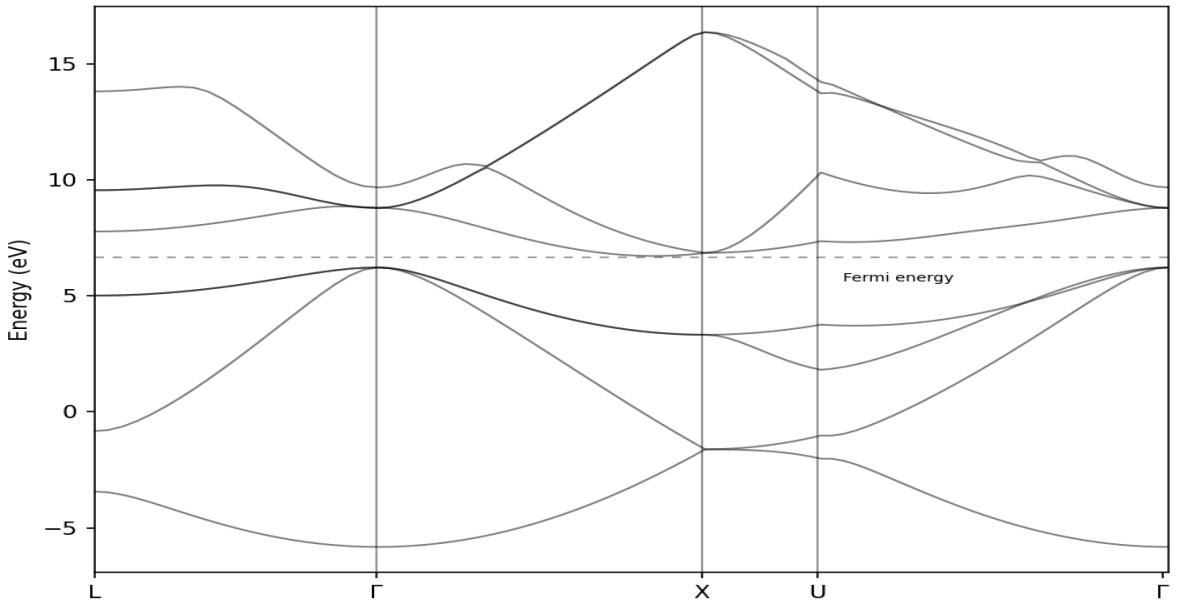
Primitive Brillouin Zone

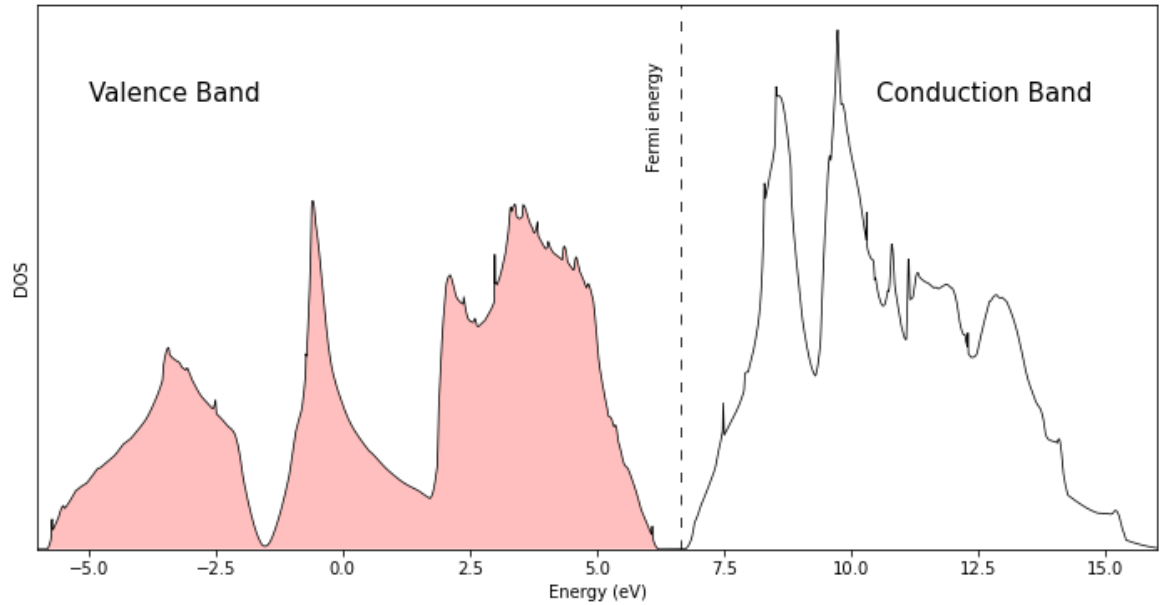


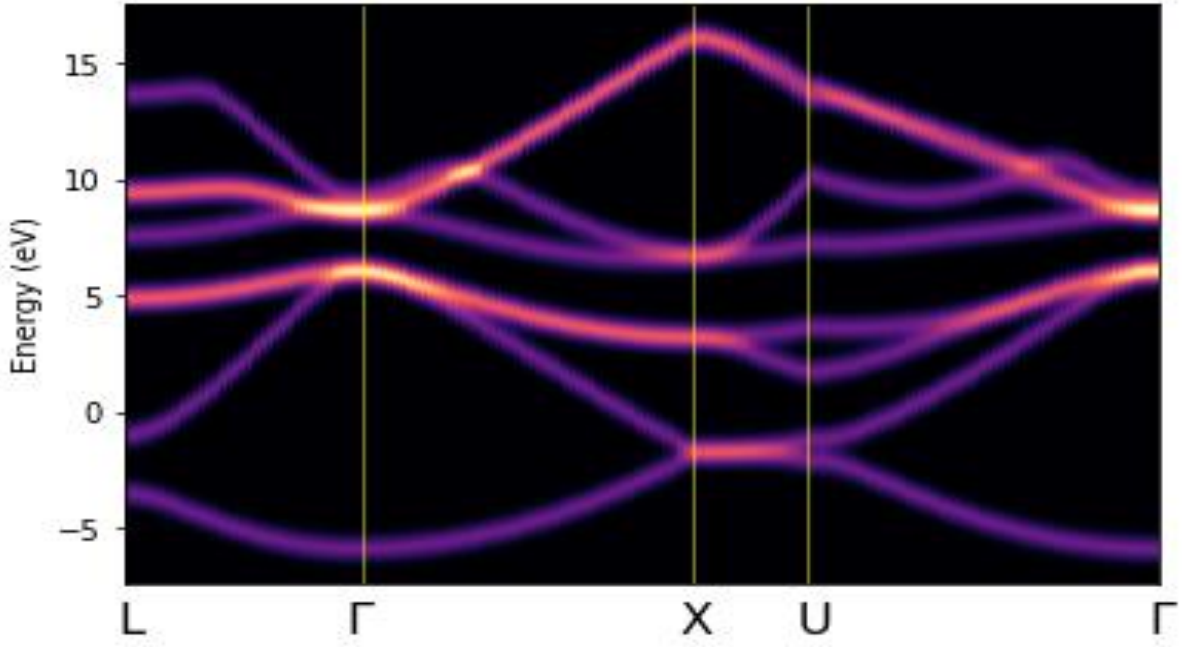


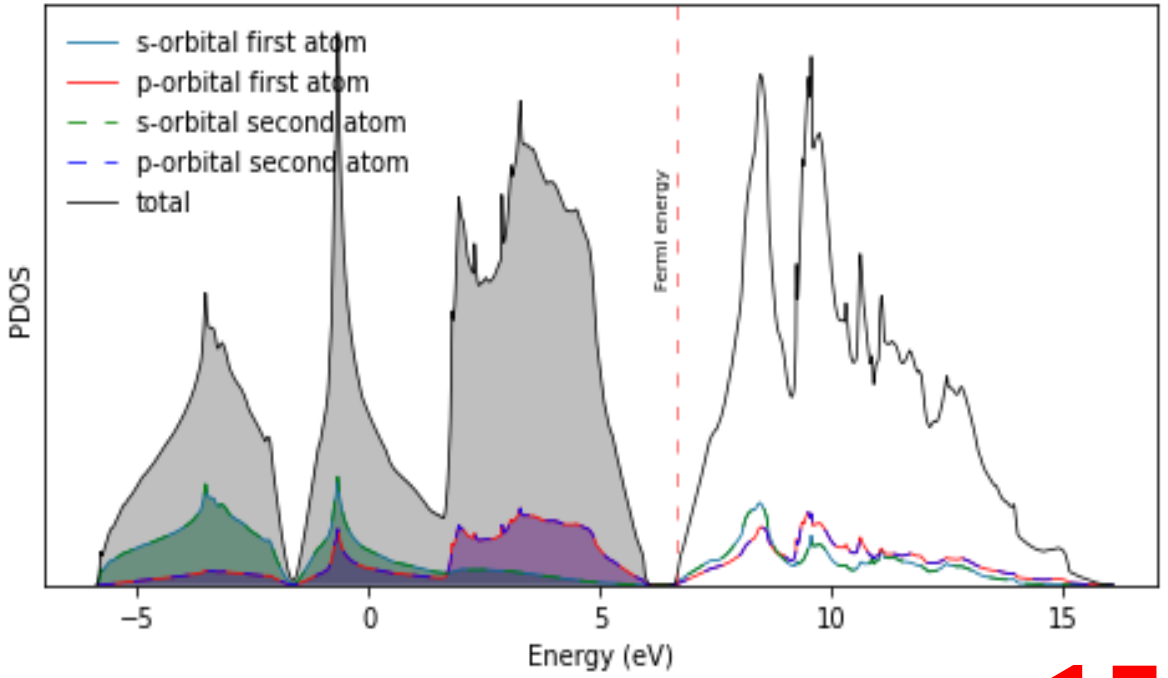


Visualization of Si, First Brillouin zone, Convergence test on ecutwfc and on k-points





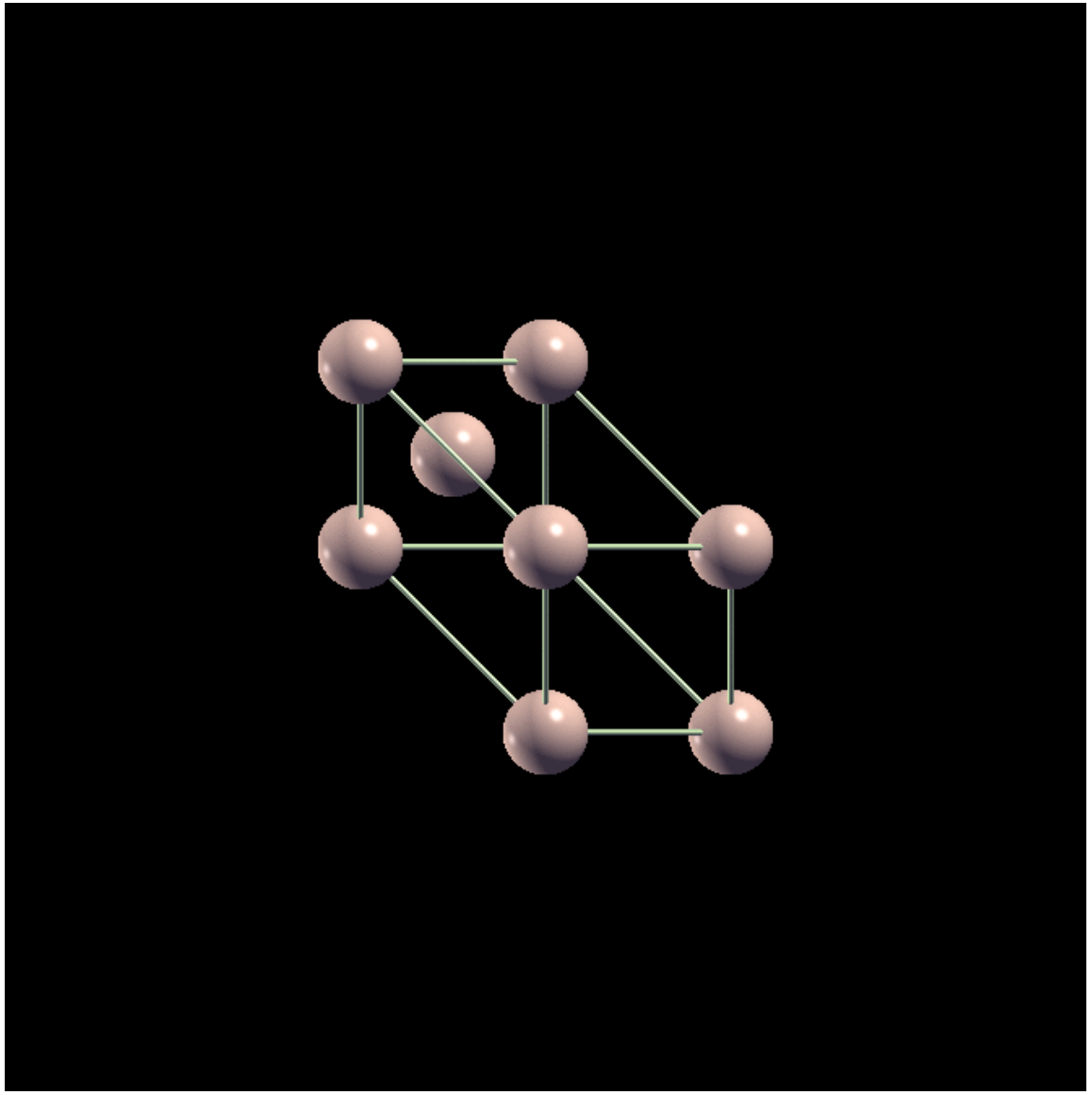


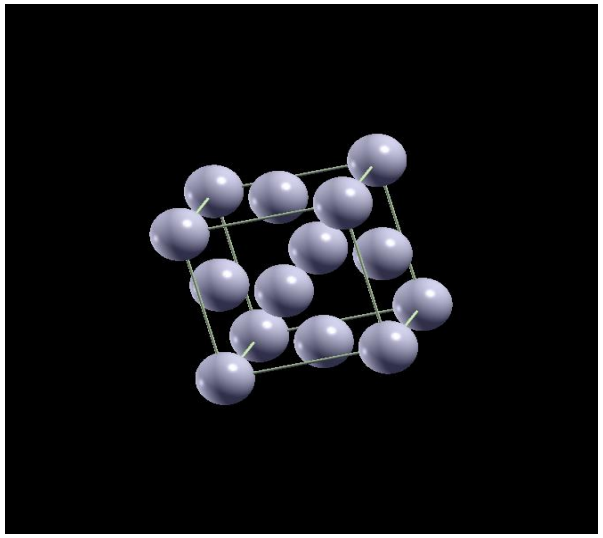


Band Structure, k-resolved BS, Density of State and Partial Density of State of Si

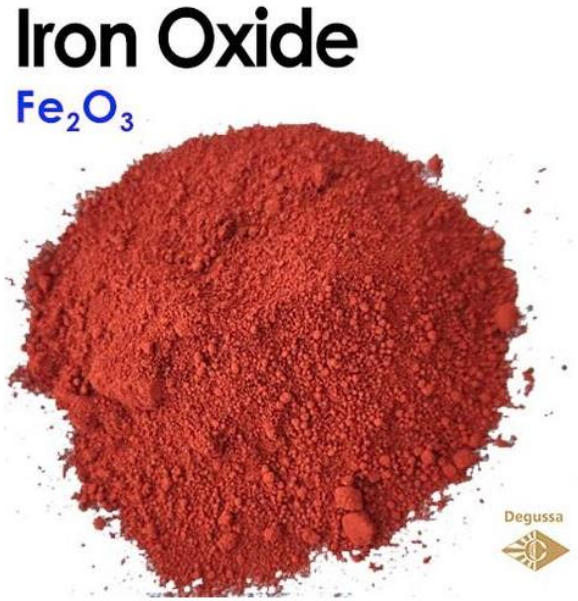
Accoustic and optic frequencies obtained with EPW and the optical phonon eigen displacement of Si

```
     Dielectric Tensor:

         13.997813420379          0.000000000000          0.000000000000
          0.000000000000         13.997813420379         -0.000000000000
          0.000000000000         -0.000000000000         13.997813420379

     Effective Charges E-U: Z_{alpha}{s,beta}

     atom #    1
         -0.074334001820         -0.000000000000         -0.000000000000
         -0.000000000000         -0.074334001820         -0.000000000000
         -0.000000000000          0.000000000000         -0.074334001820
     atom #    2
         -0.074334001820          0.000000000000         -0.000000000000
          0.000000000000         -0.074334001820         -0.000000000000
         -0.000000000000         -0.000000000000         -0.074334001820

     Diagonalizing the dynamical matrix

     q = (    0.000000000   0.000000000   0.000000000 )

 **************************************************************************
     freq (    1) =       0.082904 [THz] =       2.765383 [cm-1]
(  0.554318  0.000000 -0.439012  0.000000 -0.000343  0.000000 )
(  0.554318  0.000000 -0.439012  0.000000 -0.000343  0.000000 )
     freq (    2) =       0.082904 [THz] =       2.765383 [cm-1]
( -0.002010  0.000000 -0.003090  0.000000  0.707097 -0.000000 )
( -0.002010  0.000000 -0.003090  0.000000  0.707097 -0.000000 )
     freq (    3) =       0.082904 [THz] =       2.765383 [cm-1]
(  0.439008  0.000000  0.554309  0.000000  0.003671  0.000000 )
(  0.439008  0.000000  0.554309  0.000000  0.003671  0.000000 )
     freq (    4) =      15.548935 [THz] =     518.656641 [cm-1]
( -0.609578  0.000000  0.328722 -0.000000 -0.142676  0.000000 )
(  0.609578 -0.000000 -0.328722  0.000000  0.142676  0.000000 )
     freq (    5) =      15.548935 [THz] =     518.656641 [cm-1]
( -0.355148  0.000000 -0.591732  0.000000  0.154022  0.000000 )
(  0.355148  0.000000  0.591732  0.000000 -0.154022  0.000000 )
     freq (    6) =      15.548935 [THz] =     518.656641 [cm-1]
(  0.047795  0.000000 -0.204438  0.000000 -0.675219  0.000000 )
( -0.047795  0.000000  0.204438  0.000000  0.675219  0.000000 )
 **************************************************************************
```

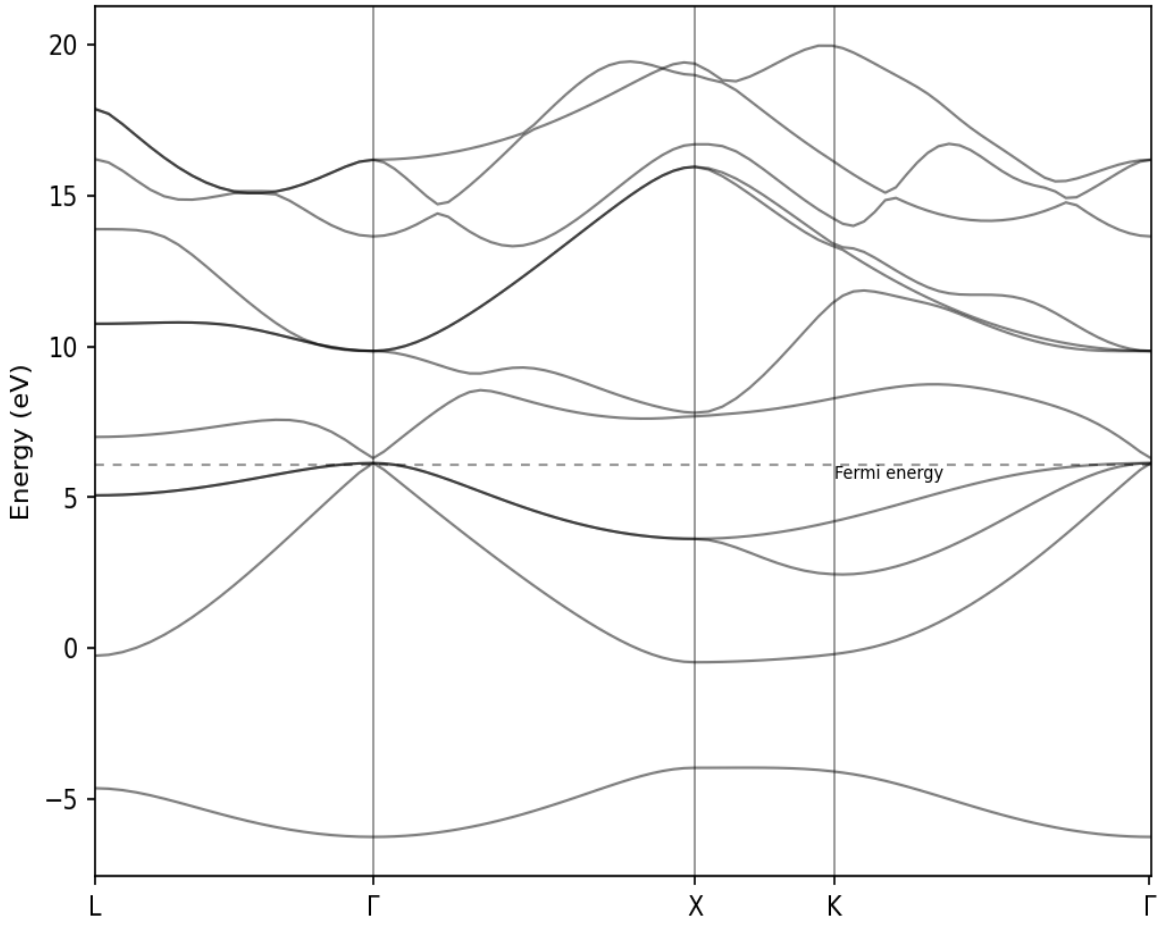


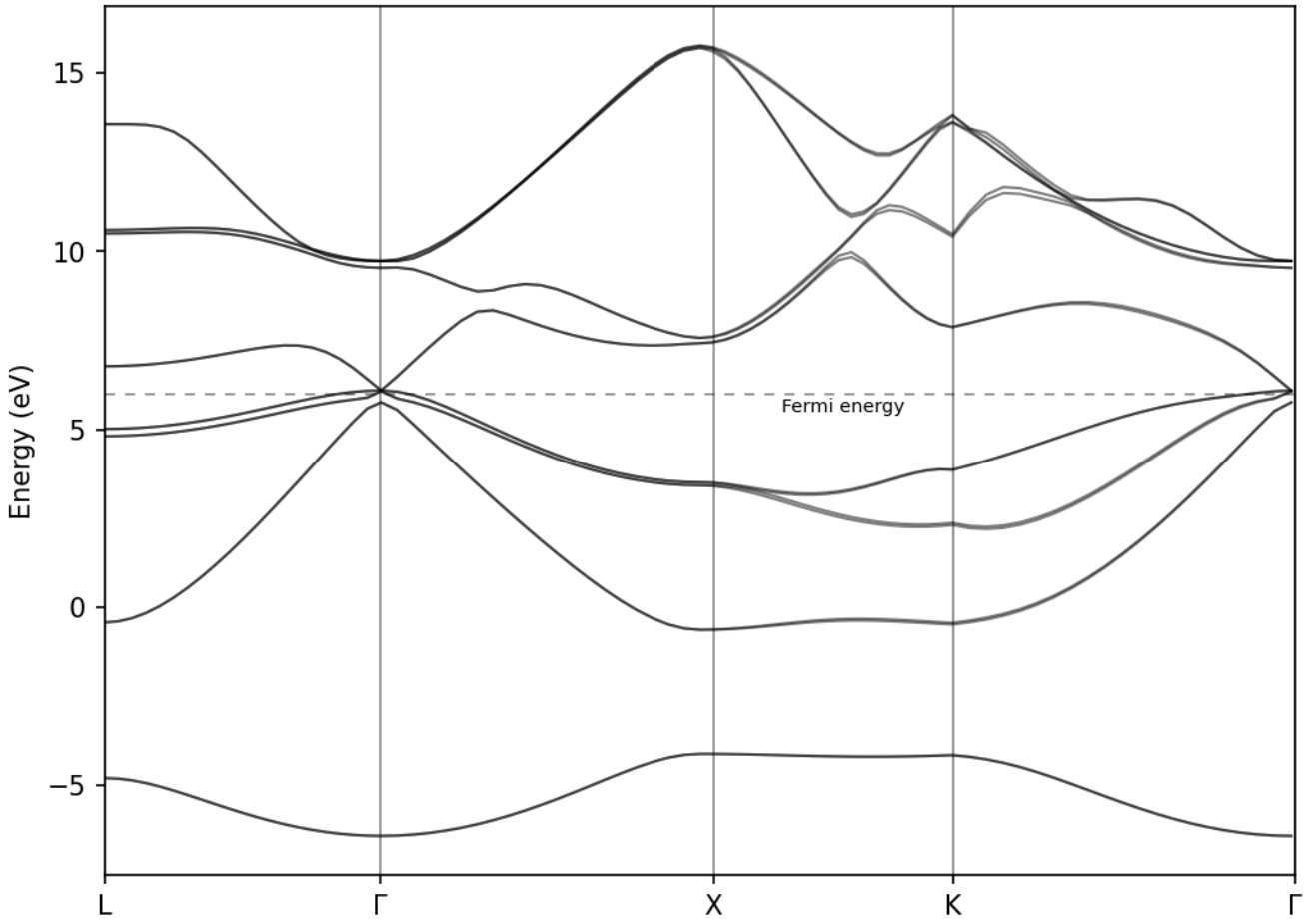


Case of: Ni, GaAS, FeO and Cu

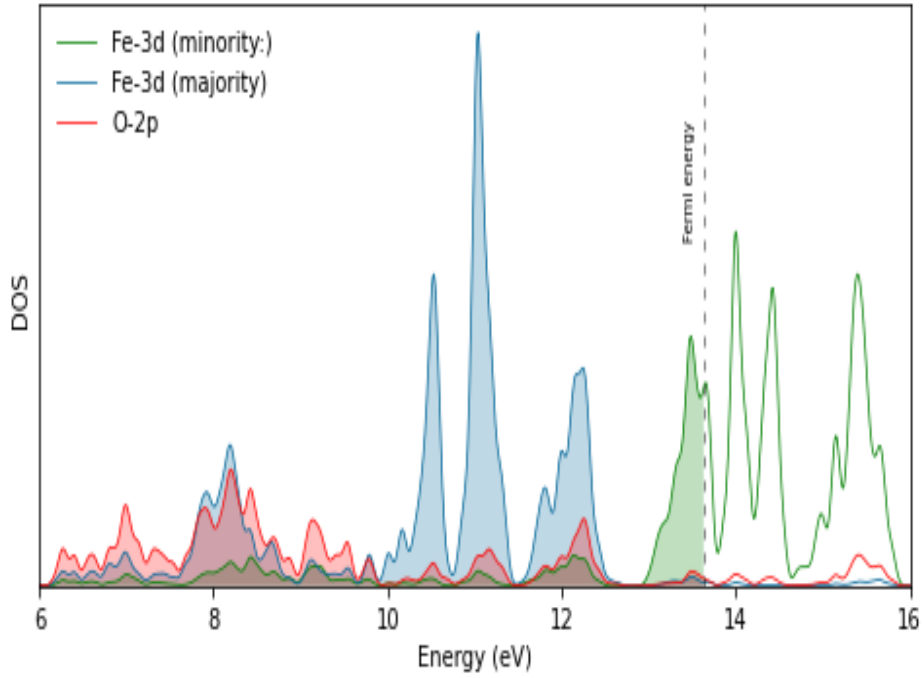


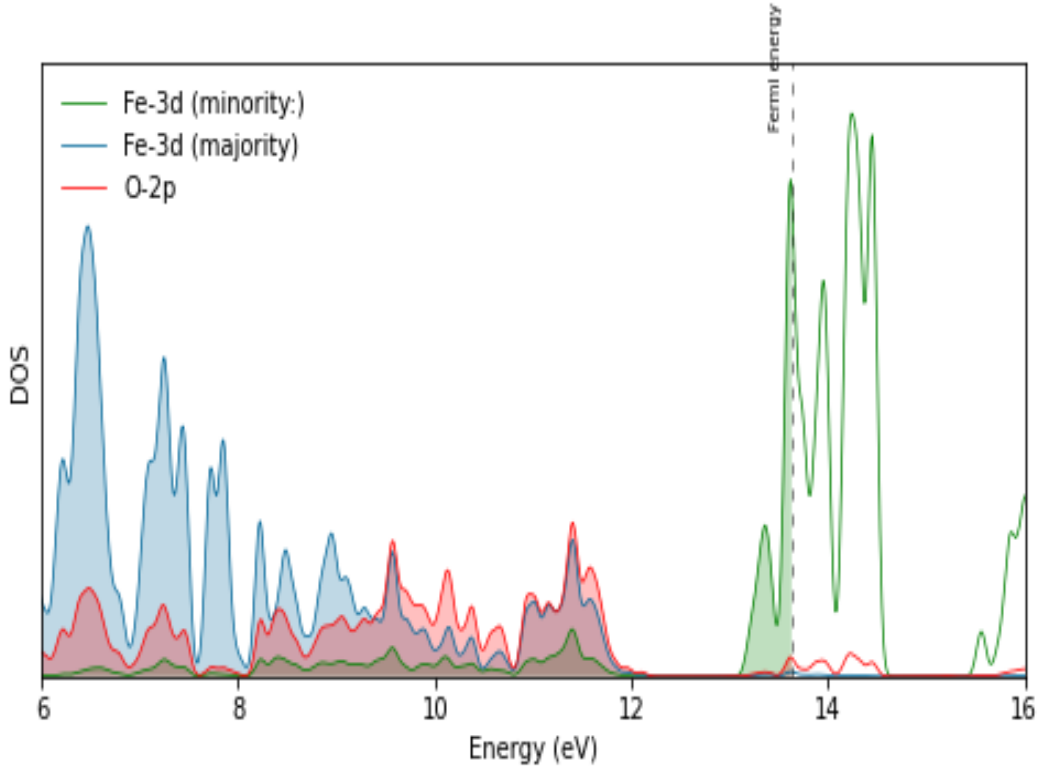
Spin orbit coupling on GaAS



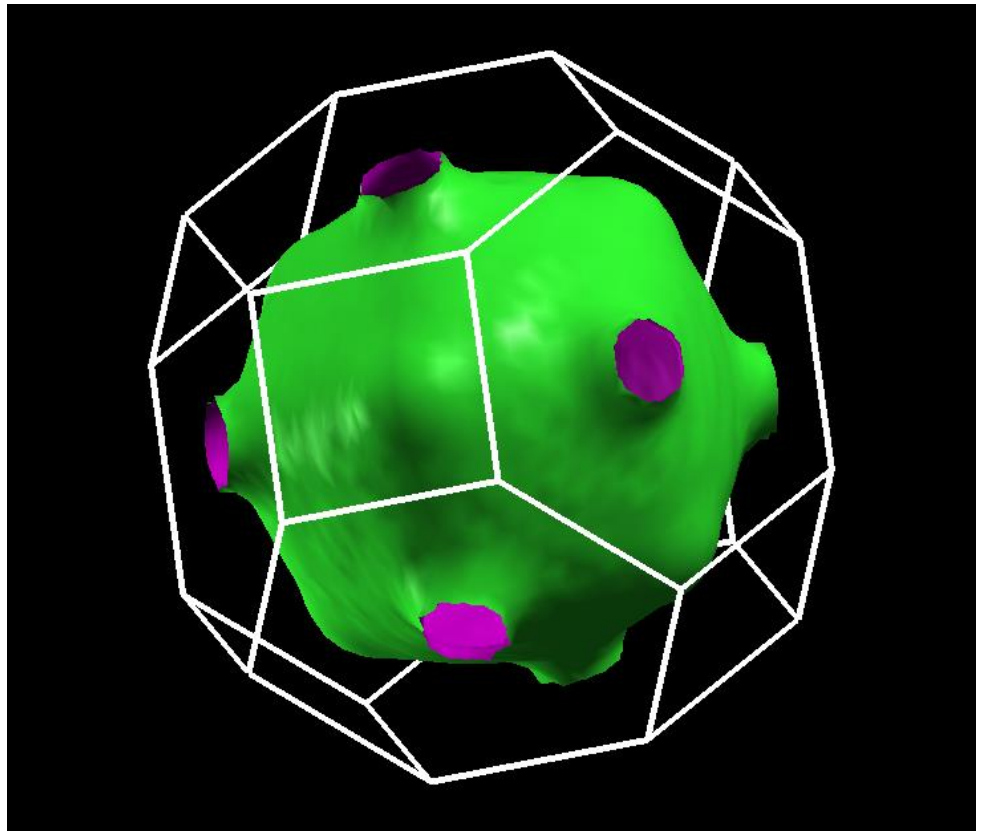


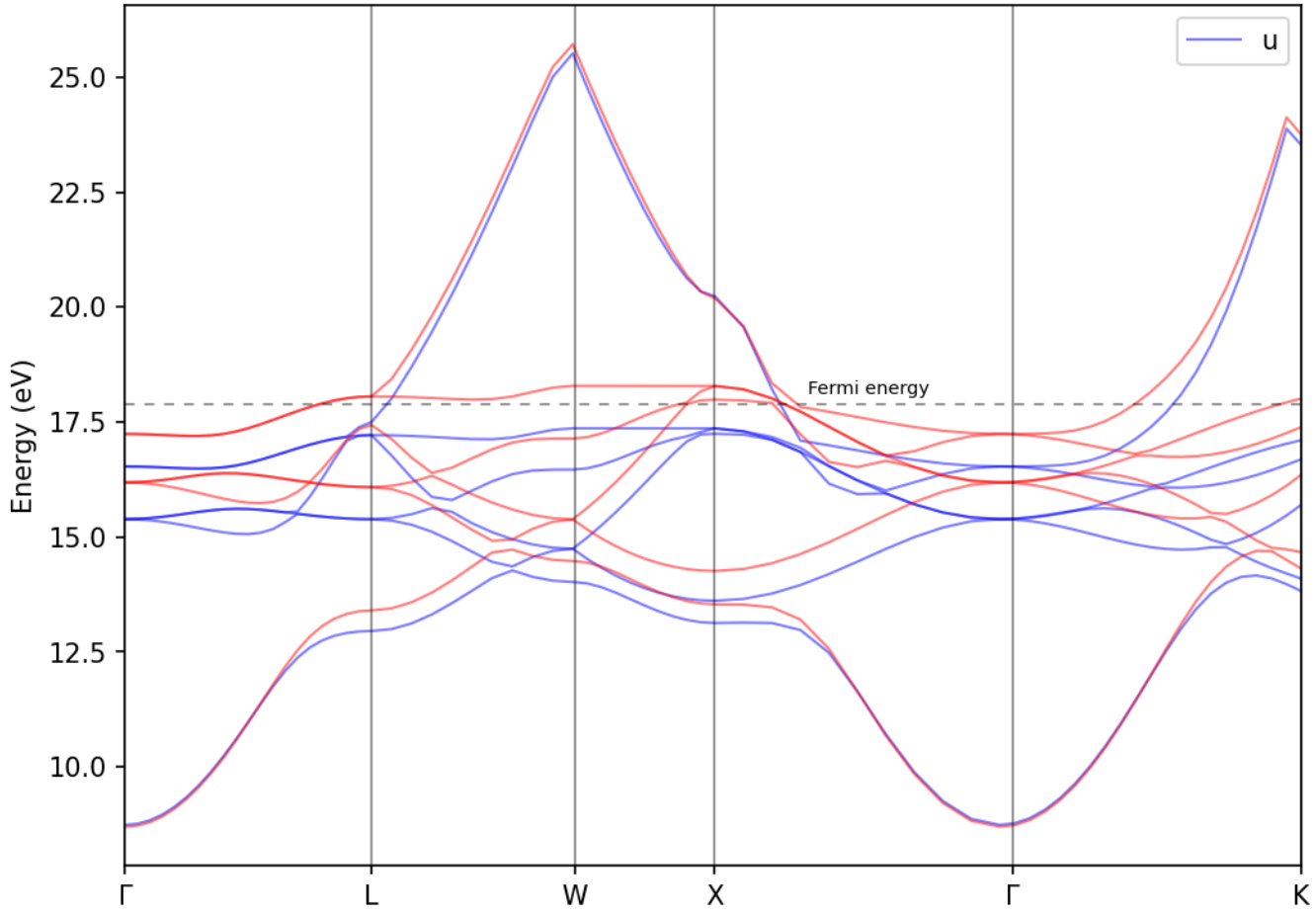
Hubbard correction on FeO: DFT+U



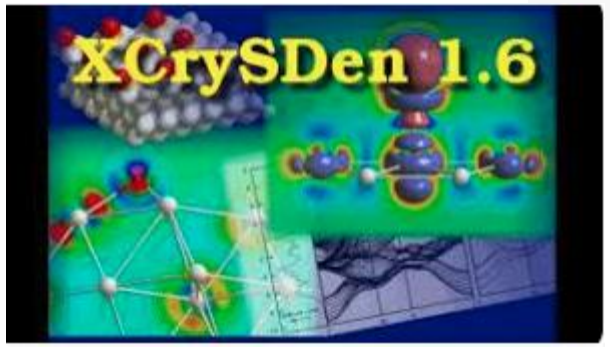


Fermi surface of Cu and Spin-polarized DFT on Ni





SOFTWARE PACKAGES



ABINIT

ABINIT allows one to study, from first-principles, systems made of electrons and nuclei (e.g. periodic solids, molecules, nanostructures, etc.), on the basis of Density-Functional Theory (DFT) and Many-Body Perturbation Theory. Beyond the computation of the total energy, charge density and electronic structure of such systems, ABINIT also implements many dynamical, dielectric, thermodynamical, mechanical, or electronic properties, at different levels of approximation.

YAMBO

Yambo is an *ab initio* code for calculating quasiparticle energies and optical properties of electronic systems within the framework of many-body perturbation theory and time-dependent DFT.

Yambo is a plane-wave code that is particularly suited for calculations of periodic bulk systems

QUANTUM ESPRESSO

Quantum ESPRESSO is an integrated suite of open-source computer codes for quantum simulations of materials using state-of-the-art electronic-structure techniques, based on density-functional theory, density-functional perturbation theory, and many-body perturbation theory, within the plane-wave pseudopotential and projector-augmented-wave approaches.

FEYNMAN DENSITY MATRIX APPROCHES

Aim: (FEYNMAN + DMA) Versus (DFT)

Feynman approach ----------Propagator

Density matrix Approach ----------Wave function

Density Functional Theory----------Electronic density

THANKS FOR YOUR KIND ATTENTION